(12) EUROPEAN PATENT APPLICATION

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(54) **Dispersion method and dispersing apparatus using supercritical state**

(57)   A dispersion method for uniformly dispersing solid or liquid fine particles in a solvent by utilizing a supercritical fluid, and a dispersing apparatus thereof. A dispersoid of a solid, a liquid or the like is mixed with a solvent, and this mixture is fed to a supercritical vessel. A supercritical solvent is then fed to the supercritical vessel. This supercritical solvent is heated and compressed to a level of higher than the critical temperature and the critical pressure to convert it to a supercritical fluid. Then, the mixture and the supercritical fluid are stirred and mixed. The obtained supercritical mixture is released to atmospheric pressure in an explosion-crashing tank. By such an operation, the dispersoid is efficiently dispersed in the solvent.

FIG. 1

(B) supercritical solvent

• supercritical solvent
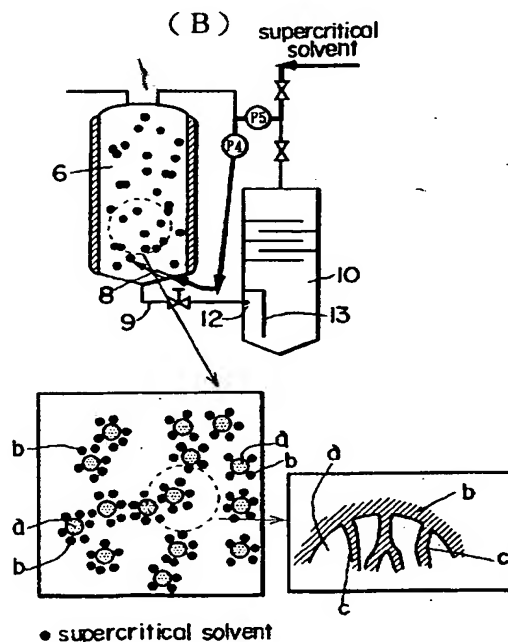
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Description

BACKGROUND OF THE INVENTION

(1) Technical Field to which the Invention belongs

The present invention relates to a dispersion method, for example, a dispersion method for a solid-liquid system wherein a solid (fine particles) and a liquid are mixed and dispersed, a dispersion method for a liquid-liquid system wherein a liquid and a liquid are mixed and emulsified, and a dispersion method for a solid-liquid (water)-liquid (organic solvent) system, particularly to a dispersion method characterized by carrying out the dispersion by using a supercritical solvent in a supercritical state as a dispersing means; and a dispersing apparatus therefor.

(2) Prior Art

There have been employed a kneader, a roll mill, a medium-dispersing machine and the like to disperse a solid dispersoid used as a material for coatings, ink, ceramics, cosmetics, foods and the like, or a homogenizer and the like to emulsify a liquid dispersoid. Usually in such processing, shearing force or the like is mechanically applied to particles to be dispersed to finely divide the particles, whereby there have been drawbacks that the processing time is long and the washing of the apparatus after the processing is troublesome.

Further, to improve such dispersion methods, there have been proposed a dispersion method wherein a solvent and a dispersoid are mixed in a supercritical state and the solvent is rapidly expanded to finely divide the dispersoid, and then the fine particles are blown into a solvent such as varnish, toluene or the like. However, in such a method, when the fine particles are blown into the solvent, reagglomeration is likely to take place, whereby the dispersed conditon will deteriorate.

SUMMARY OF THE INVENTION

The present invention is intended to utilize the characteristics of a supercritical fluid which is capable of continuously and rapidly changing the density from a gaseous density to a liquid density by changing the pressure and temperature. An object of the present invention is to provide a dispersion method and a dispersing apparatus by which a solid or liquid dispersoid can be efficiently dispersed without causing the above-mentioned drawbacks, preferably to provide a dispersion method and a dispersing apparatus using the supercritical state, which can be operated by computer control.

According to the present invention, the above objects can be accomplished by providing a dispersion method using the supercritical state which comprises feeding a mixture of a dispersoid and a solvent into a supercritical vessel, feeding a supercritical solvent into the supercritical vessel, heating and compressing the supercritical solvent to convert it from a gaseous phase state to a supercritical fluid, mixing the mixture and the supercritical fluid in the supercritical vessel, then introducing the supercritical mixture of the mixture and the supercritical fluid to an explosion-crashing tank, by which the supercritical mixuture is jetted to atmospheric pressure and at the same time the supercritical mixture undergoes collision in the explosion-crashing tank, for dispersion of the dispersoid into the solvent, and a dispersing apparatus.

In the present invention, the supercritical solvent represents a solvent for the preparation of the supercritical state. The supercritical state and the supercritical fluid, are not only a so-called supercritical state and supercritical fluid which exceed the critical state and critical fluid, but also a semi-supercritical state and semi-supercritical fluid which are slightly less than the critical state and critical fluid, but can be deemed to be substantially the same as the above supercritical state and supercritical fluid, since the change of phase transformation takes place in an extremely short period of time.

Further, in the present invention, the explosion-crashing is an operation by which the following effects are caused:

(1) when the dispersoid is porous particles, the supercritical fluid penetrates into pores or narrow-spaces thereof and the pressure is rapidly reduced to cause rapid cubical expansion, by which the porous particles are crashed and dispersed,

(2) by jetting the dispersion under the supercritical state from a nozzle having pores or slits of narrow spaces at a sonic speed or a flow velocity above it, by which a high shear deformation action is applied to the dispersoid for crashing and dispersion, and

(3) the jetted liquid is collided against a wall surface or the like by the inertia force corresponding to the mass of fine particles of the jetted liquid, by which impact action is applied to the dispersoid for crashing and dispersion.

BRIEF EXPLANATION OF THE DRAWINGS

Figs. 1(A) to 1(D) show dispersion methods of a solid (fine particles)-liquid system. Fig. 1(A) is an explanatory drawing showing a step for charging a slurry. Fig. 1(B) is an explanatory drawing showing a step for preparing a supercritical state. Fig.1(C) is an explanatory drawing showing a stirring and mixing step when a jet-stirring is employed. Fig.1(D) is an explanatory drawing showing an explosion-crashing step when an explosion-crashing nozzle and a vertical plate-like

collision portion are employed.

Figs. 2(A) to 2(D) show stirring means. Fig.2(A) is an explanatory drawing showing a jet stirring. Fig.2(B) is an explanatory drawing showing an ultrasonic stirring. Fig. 2(C) is an explanatory drawing showing a vibration plate actuated by an external shifting magnetic field. Fig.2(D) is an explanatory drawing showing rotation blades actuated by an external shifting magnetic field.

Figs. 3(A) to 3(C) show collision portions of the explosion-crashing vessel. Figs.3(A) and 3(B) are explanatory drawings showing collision plates each provided with a fence. Fig.3(C) is an explanatory drawing showing a case of a countercurrent collision.

Figs. 4(A) to 4(C) show operation routes of temperature and pressure for the preparation of a supercritical state from a supercritical solvent which is in a gaseous state at room temperature and ordinary pressure. Fig.4(A) shows a step for temperature-pressure operation. Fig.4(B) shows an illustration in a density-pressure isothermic chart in the step for temperature-pressure operation. Fig.4(C) shows an illustration in a density-temperature isotactic chart in the step for temperature-pressure operation.

Figs. 5(A) to 5(C) show operation routes of temperature and pressure for the preparation of a supercritical state from a supercritical solvent which is in a liquid state at room temperature and ordinary pressure. Fig.5(A) shows a step for temperature-pressure operation. Fig.5(B) shows an illustration in a density-pressure isothermic chart in the step for temperature-pressure operation. Fig.5(C) shows an illustration in a density-temperature isotactic chart in the step for temperature-pressure operation.

Figs. 6(A) to 6(D) show dispersion methods for a liquid-liquid system according to the present invention. Fig. 6(A) is an explanatory drawing showing a step for charging an emulsion. Fig.6(B) is an explanatory drawing showing a step for preparing a supercritical state.Fig.6 (C) is an explanatory drawing showing a stirring and mixing step when a jet-stirring is used. Fig.6(D)is an explanatory drawing showing an explosion-crashing step when an explosion-crashing nozzle and a vertical plate-like collision portion are used.

Fig. 7 is an explanatory drawing showing an embodiment of a dispersing apparatus according to the present invention.

Figs. 8(A) to 8(D) are explanatory drawings showing dispersed conditions in the examples wherein dispersion is carried out in accordance with the present invention or the comparative examples.

Fig.9 is a chart showing particle size distributions in the examples wherein dispersion is carried out in accordance with the present invention or the comparative examples.

PREFERRED EMBODIMENTS OF THE INVENTION

The principle of the present invention will be explained below with reference to the drawings. Fig.1 shows a case where the dispersoid is solid fine particles and such fine particles are dispersed in a liquid solvent. Here, solid fine particles include, for example, ultrafine particles such as pigments, ceramics material powder or magnetic particles, and sometimes also a few types of fine particles. The liquid solvent includes water, an organic solvent or the like which forms a continuous phase in a dispersion. A mixture of them under suspended condition (rough dispersion) (hereinafter referred to as a "slurry") is charged into a supercritical vessel 6 from a feeding inlet 30 (Fig.1(A)). At this time, appropriate agents, e.g., a dispersant such as a polymer surfactant, may be incorporated beforehand. At this stage, it is believed that the solid fine particles (a...) are in a so-called agglomerate state of fine particles wherein generally plural or many fine articles form aggregates, and such agglomerate state fine particles are suspended in a solvent.

The above slurry may be preliminarily dispersed by a preliminary dispersing apparatus before feeding it into the above vessel, or may be directly fed into the vessel without preliminary mixing, depending on the properties of the dispersoid.

Then, the supercritical vessel 6 is filled with the supercritical solvent from a feeding inlet (nozzle) 8 thereof. The supercritical solvent is heated and compressed by a heating and compressing means such as a pump and a heater, equipped for the vessel for the preparation of the supercritical fluid by bringing the conditions above the critical temperature and the critical pressure (Fig.1(B). The supercritical fluid (b...) thus obtained has a higher diffusion coefficient and a smaller surface tension as compared with a liquid solvent such as water or an alcohol, and is therefore likely to be wetted and capable of rapidly penetrating into the aggregate of the fine particles (a...). Further, since the interaction (attraction) between the fine particles and the supercritical fluid is larger than the interaction (attraction) between the fine particles to one another which constitute the aggregate, the aggregate of the fine particles is crashed and divided into individual particles, resulting in the progress of primary particle formation, whereby the dispersion of the fine particles is accelerated. At this time,when the fine particles have pores (c), since the supercritical fluid has a high diffusion coefficient and a small surface tension as mentioned above, the supercritical fluid impregnates into the pores (c) of the fine particles (a) as shown in an enlarged figure.

Then, to further progress the formation of primary particles and the impregnation between the particles or into the pores thereof, the above supercritical mixture of the slurry and the supercritical fluid in the supercritical vessel is stirred by a stirring means (Fig.1(C)). As the stirring means, various methods may be used. Preferably, the stirring means has a sealed structure such that a stirring shaft or the like does not extend throughout

the supercritical vessel. In the stirring means as shown in Figs.1(A) to 1(D) and 2(A), a jet nozzle 8 is disposed toward the inside of the supercritical vessel, a circulation port 31 formed in the supercritical vessel 6 is connected to the nozzle 8 through a pump P4,and the supercritical mixture is circulated and compressed by the pump and jetted from the jet nozzle 8 into the supercritical vessel to form a circulation flow within the vessel, carry out the stirring and mixing and accelerate the homogenization.

In the stirring means as shown in Fig.2(B), ultrasonic wave is applied into the supercritical vessel 6 to stir the mixture in the vessel and make it uniform. An ultrasonic wave applying aperture 32 is provided to the vessel so that it is connected to an ultrasonic-generating means not shown in the drawing.

Further, an electromagnetic coil which generates a shifting magnetic field, may be provided outside the supercritical vessel 6 to stir the mixture in the vessel. In the example as shown in Fig.2(C), a vibration-generating device 34 which is generated by an external shifting magnetic field and has a vibration plate 33 within the vessel, is provided so that the vibration plate 33 is vibrated by actuating the vibration-generating device 34 by an electromagnetic coil 35 which generates an external shifting magnetic field.

In the example as shown in Fig. 2(D), a rotor 37 which is rotated by an external rotatable shifting magnetic field and has rotation blades 36, is provided within the supercritical vessel so that the rotation blades 36 are rotated by actuating the rotor 37 by an electromagnetic coil 38 which generates an external shifting magnetic field.

The supercritical mixture stirred and mixed by various stirring means as mentioned above, is discharged from a flow out port 39 of the supercritical vessel 6, introduced into an explosion-crashing tank 10 through a line 9 which is connected to the flow out port 39, jetted within the explosion-crashing tank 10 by releasing it to atmospheric pressure, and collided against a collision portion to accelerate the dispersion by impact action (Fig.1(D)). A jetting port 12 of the explosion-crashing tank 10 may have the structure of an explosion-crashing nozzle 40 having slits or pores with an appropriate inner diameter (in Fig.3(A)), or an explosion-crashing window 41 having an appropriate aperture area (in Fig.3(B)). The line 9 which connects the explosion-crashing nozzle or the like to the flow out port 39 of the supercritical vessel 6, is preferably heated by a heater given thereto (not shown in the drawing).

As the ones shown as the collision portion in Figs.3 (A) and 3(B), formed is a collision plate 13 which surrounds the forward portion of the nozzle, window or the like and opens downwardly. In the case of the nozzle 40, a vertical plate-like collision plate 13a is formed so that it is located vertically to the jetting direction of the nozzle 40. In the case of the explosion-crashing window 41, a semi-spherical plate-like collision plate 13b is formed so

that it forms semi-sphere to the window 41. In both cases, the dispersion jetted from the nozzle or the like is collided in a substantially vertical direction to the wall surface so that the impact force can act effectively.

As the collision portion, no plate-like body may be used. In such a case, as shown in Fig.3(C), explosion-crashing nozzles 40, 40 are disposed oppositely within the explosion-crashing tank 10, the line 9 from the supercritical vessel 6 is divided into two branches and connected to the espective nozzles 40, 40, and then dispersions are jetted oppositely from respective nozzles 40, 40, to collide the liquids to each other, whereby the dispersion can be accelerated by the impact at the time of collision. Here, the explosion-crashing nozzles 40,40 are disposed within a hood 42 in the explosion-crashing tank 10, and the dispersion jetted from the nozzles are collided to each other and then low downwardly without scattering to the circumference.

In the explosion-crashing tank 10, since the volume of the supercritical solvent in the aggregate of the fine particles is rapidly expanded as mentioned above, the fine particles are further divided into individual particles under the condition of primary particles. At that time, if the fine particles have pores, the fine particles themselves are further crashed and dispersed by the cubical expansion of the supercritical solvent impregnated into the pores.

In the above steps, the heating and compressing operation to covert the supercritical solvent to a supercritical fluid, is prerferably an operation of phase transforming the supercritical solvent from a gaseous phase state to a supercritical state. Figs. 4(A) to 4(C) show operation routes of temperature and pressure for the preparation of a supercritical state from a supercritical solvent which is in a gaseous state at room temperature and ordinary pressure. Fig.4(A) shows a step for temperature-pressure operation. Fig.4(B) shows an illustration in a density-pressure isothermic chart in the step for temperature-pressure operation. Fig.4 (C) shows an illustration in a density-temperature isotactic chart in the step for temperature-pressure operation. The thick solid lines in these drawings indicates various operation steps.

In the above drawings, the operation step (1) indicated by a route number 1 -> 2 -> 5 shows a change from a gas to a liquid by the route 1 -> 2, and a change from a liquid to a supercritical fluid by the route 2 -> 5. With respect to the relation between the state of the phases and the dispersion of the solid particles in this case, when the line crosses the vapor-liquid equilibrium range, the surface of particles is wetted with a liquid, whereby the supercritical fluid hardly impregnates into narrow spaces or the like of such wetted particles. As a result, the impregnation of the supercritical solvent into the spaces of aggregate of solid particles or the pores of solid particles, is mainly carried out by molecular diffusion by the solvent such as an organic solvent in the slurry, and if the supercritical solvent reaches the super-

critical state, the effects of the supercritical fluid hardly extend to the spaces of the aggregate of solid particles or the pores of solid particles. Accordingly, the formation of the primary particles by the dispersion or explosion-crashing effect in the supercritical state, will be insufficient as mentioned above.

In an operation of a route 1 -> 3 -> 5 as shown in the operation step (2),the supercritical solvent is compressed in the route 1 -> 3 in a gaseous state as it is, and continuously transformed into a supercritical fluid in the route 3 -> 5. In such a case, since the supercritical solvent is continuously transformed from a gas to a supercritical fluid, the impregnation of the supercritical fluid into the spaces between the aggregate of solid particles or the pores of solid particles is excellent.

In an operation of a route 1 -> 4 -> 5 as shown in the operation step (3), the supercritical solvent is compressed in the route 1 -> 4 in a gaseous state as it is, and continuously transformed to a supercritical fluid in the route 4 -> 5. In such a case, the impregnation of the supercritical fluidis excellent like the above operation step (2), and it is possible to control elements such as pressure, temperature and density, effectively by a computer, whereby most preferred conditions for dispersion of the solid particles can be selected and the dispersion operation can be carried out in a short period of time. As the control of the dispersion in a solid-liquid system, for example, firstly the density of the supercritical fluid is made low for easy impregnation, and then the pressure is raised to make the density high for increase of the wettability, followed by the release of the fluid to atomospheric pressure in the explosion-crashing tank.

Figs.5(A) to 5(C) show operation routes for the preperation of a supercritical state from a supercritical solvent which is in a liquid state at room temperature and ordinary pressure. Like Figs.4(A) to 4(C), Fig.5(A) shows a step for temperature-pressure operation, Fig.5(B) shows an illustration in a density-pressure isothermic chart in the step for temperature-pressure operation, and Fig.5(C) shows an illustration in a density-temperature isotactic chart in the step for temperature-pressure operation. As the operation steps in such cases, as indicated by the route 1 -> 2 -> 3 or the route 1 -> 4 -> 3,firstly the temperature is raised to a level higher than the critical temperature to carry out the transformation of the supercritical solvent from a liquid to a gas, and then pressure operation is carried out so that the gas is transformed to a supercritical fluid. At that time,the fluid is subjected to a gas-liquid phase transformation. However, this phase transformation is a phase transformation wherein the density becomes small, and believed to cause no effect to the penetration into the pores of solid particles or into the spaces of aggregate of solid particles.

As mentioned above, there are various operation steps to convert a supercritical solvent into a supercritical state. For example, a step which undergoes a phase transformation from a gas to a liquid, is a phase trans-

formation of increasing the density, whereas a step which undergoes a phase transformation from a liquid to a gas, is a phase transformation of decreasing the density. The phase transformation of decreasing the density, does not prevent the supercritical fluid from impregnating into the spaces of the aggregate of solid particles or into the pores of the particles. Therefore, in the present invention, a heating and compressing means is operated so that transformation to the supercritical fluid is carried out through a gaseous state.

Figs.6(A) to 6(D) show methods for dispersing droplets wherein a liquid dispersoid is dispersed in a solvent. Here, a liquid solute for dispersion, such as fat balls, is suspended in a solvent such as water or an organic solvent (rough dispersion). Such a suspension is charged as various mixtures of a liquid-liquid system (hereinafter referred to as an emulsion) such as a water-organic solvent system, an organic solute-organic solvent system, two or more organic solutes-organic solvent system, into the supercritical vessel 6 from a feeding inlet 30 (Fig.6(A)). At this time, additives such as a dispersant and a reagent, may be added beforehand.

Then, the supercritical vessel 6 is filled with the supercritical solvent from the feeding inlet 8 of the vessel , the temperature and pressure are adjusted to the desired values by a heating and compressing means such as a pump or a heater, to prepare the supercritical state (Fig. 6(B)). The supercritical fluid obtained by such an operation generally has a higher affinity with a solute for dispersion as compared with water, and therefore there are two conceivable cases within the supercritical vessel, i.e., a case wherein droplets of a mixture are formed under such a condition that the supercritical fluid (b..) is dissolved in a solute for dispersion (d...) and dispersed in the solvent such as water or an organic solvent, and the droplets are in a supercritical state, as shown in the enlarged figure of thee part (B-1) in Fig.6(B); and a case wherein the supercritical fluid, solute for dispersion and the solvent such as water are in a supercritical state under uniform conditions, as shown in the enlarged figure of the part (B-2) in Fig.6(B).

Then, stirring and mixing within the supercritical vessel 6 is carried out by a stirring means (Fig.6 (C)). This figure shows a means in which a supercritical mixture is circulated and compressed by a pump (P4) and then jetted in the vessel from the jet nozzle 8. However, various means as shown in Fig.2(A) to (D) can be used. By such an operation, in the state as indicated in the part (B-1) of Fig .6(B), the formation of fine particles is carried out so that the droplets have a diameter of from submicron to a few micron meter order. In the state as indicated in the part (B-2) of Fig.6(B), uniformity is further accelerated, and better dispersion condition can be achieved.

The supercritical mixture stirred and mixed as above is introduced from the flow out port 39 of the supercritical vessel 6 to an explosion-crashing tank 10

and jetted into the explosion-crashing tank 10 from the explosion-crashing nozzle or window of the tank (Fig.6(D)). At this time, in the condition as shown in the part (B-1) of Fig.6(B), the volume of the supercritical solvent in the droplets rapidly increases, whereby the droplets are finely divided for acceleration of the dispersion of the solute. Further, in the condition as shown in the part (B-2) of Fig. 6(B), by rapidly evaporating and dispersing the supercritical solvent, the dispersion in a uniform condition becomes an excellent dispersion in such a condition that extremely fine droplets of the solute exist in the liquid. By the impact action of collision of the dispersion against the collision portion as indicated in Fig.3(A) to (C) disposed within the explosion-crashing tank 10, the dispersion is further accelerated. The above respective operation can be controlled by a computer, and in such a case, the operation is carried out by, for example, adjusting the supercritical fluid to a high density condition at the initial stage to sufficiently dissolve it in the solute and then releasing the fluid to atmospheric pressure in the explosion-crashing tank.

Fig.7 shows a schematic view of an example of preferred apparatuses for the dispersion system to carry out the above-mentioned dispersion methods.

In this figure,as an example when a preliminary mixing is carried out if desired, a preliminary mixing machine such as a kneading machine 1 such as a roll mill or a kneader or a planetary mixer 2, is provided. A dispersoid, a solvent, a dispersant and the like are mixed by the preliminary mixing machine, and this mixture is fed to a dispersion material controlling tank 3 by a pump P1 such as a snake pump or a screw extrusion machine. The controlling tank 3 is preferably equipped with a stirring machine 4 to prevent the precipitation or agglomeration of particles or the separation of the solute.

To the tank 3 a medium-dispersing machine 5 is connected through a valve V1 and a dispersion material liquid-feeding pump P2. The medium-dispersing machine 5 is connected to a feeding inlet 30 of a supercritical vessel 6 through a dispersion material liquid-feeding pump P3 by which compression can be made to a level of 200 atm, a flow meter M1 and a valve V2.

The supercritical vessel 6 is heated by a jacket 7 equipped with a temperature controlling means, and a supercritical solvent is fed from a jet nozzle 8. In the supercritical vessel 6, a circulation port 31 is disposed for the case of carrying out the stirring by jetting as shown in Fig.1(A) to (D), etc., and the circulation port 31 is connected to the above nozzle 8 through a valve V3, a circulation pump P4 which has a pressure-resistance to a level of 200 atm, and a flow meter M2. Further, a line which is communicated to a feeding source of the supercritical solvent, is interposed between the valve V3 and the pump P4 through a valve V4, a filter F1 and a compressor pump for compression P5.

The supercritical vessel 6 is equipped with a pressure gauge G and a thermometer T1. To the flow out

port 39, connected is a line 9 equipped with a heater for which heating is carried out by an external heater and supercooling is prevented The line 9 is connected to an explosion-crashing tank 10 through a reducing valve equipped with an actuator V6 and a flow meter M3.

Within the explosion-crashing tank 10, screen boards 11 are disposed at the upper portion, the above line is connected to a jetting port 12 of the explosion-crashing nozzle or window, and a collision plate 13 equipped with a fence is formed at the forward portion of the jetting port 12 of the explosion-crashing nozzle or window. As the explosion-crashing nozzle or the like, to prevent the clogging by freezing, a nozzle with a heater as used for the process for producing fine particles using a supercritical fluid is used.

To the explosion-crashing tank 10, a buffer tank 14 is connected for recovery of the supercritical solvent separated from the dispersion, through a filter F2 and a compressor pump for compression P6. The buffer tank 14 is connected to the above pump P5 through a valve V5. As the valves V1 to V5, preferred is a stop valve such as a ball valve with an actuator. As the filters F1, F2, and the like, a metal sintered porous body, ceramics or the like is used.

To the lower portion of the explosion-crashing tank 10, a storage tank (a deaeration tank) 15 is connected through a liquid-feeding pump P7 and a flow meter M4. The storage tank 15 is heated by a heating jacket 16 equipped with a temperature controlling means. The dispersion is stirred and mixed by a stirring machine 17. The storage tank 15 is equipped with a thermometer T2. Further, if desired, at the upper portion of the storage tank 15, a recovery apparatus which communicates to the buffer tank 14, may be provided for the recovery of the unrecovered supercritical solvent separated from the dispersion.

To the dispersion material controlling tank 3, medium-dispersing machine 5, supercritical vessel 6, explosion-crashing tank 10 and storage tank 15,provided are discharge ports each equipped with a valve, 18, 19, 20, 21 and 22, for discharging the washing liquids thereof. Further, the data of temperature obtained by the thermometers T1 and T2. the data of pressure obtained by the pressure gauge G, and the data of flow rate obtained by flow meters M1 to M4, are sent to a computer, and subjected to operation, and then signals are sent to the pumps P1 to P7, actuaters of the valves V1 to V5, temperature controllers of the heating jackets 7 and 16, the heater of the line 9, etc. for control of the liquid feeding rate of each pump, the open and shut of the valve, the heating rate of the jackets and heaters, and the like.

The operation procedures of the above systems will be explained below. In the case of a solid-liquid system, the dispersoid contains ultrafine particles such as a pigment, ceramics material powder or magnetic particles, and may sometimes contain various types of fine particles. In the case of a liquid-liquid system, there are two

cases i.e. a liquid-liquid system of water and a solute, for example, a hydrophobic liquid such as a fatty, an organic agent and a monomer, and a liquid-liquid system of an organic solvent and a solute for dispersion,insoluble in the organic solvent such as a fatty, an organic agent and a monomer. Such a dispersoid is mixed with a solvent such as water or an organic solvent, and if desired, with an agent (a dispersant for accelerating the dispersion of fine particles or a solute, or a surface modifier for imparting various functions to the surface of fine particles, a coating agent, etc.), and then adjusted to a desired concentration for a liquid-like dispersion (a slurry or an emulsion). At this stage, the above valves V1, V2 and V4 are closed, and the valves V3, V5 and V6 are opened.

Then, the valve V4 is opened (the valves V1 and V2 are closed, and the valves V3, V5 and V6 are opened),a supercritical solvent such as carbon dioxide, ethylene or a substitute for Freon, is fed to the supercritical vessel 6, explosion-crashing tank 10, buffer tank 14 and the like, to substitute the internal atmosphere by the supercritical solvent.

After the substitution treatment, the valves V3 to V6 are closed, and the valves V1 and V2 are opened. The dispersion material in the dispersion material-controlling tank 3 is fed to the medium-dispersing machine 5 by the pump P2, and mixed with a dispersoid, a solvent and an agent into a more uniform condition (if dispersion material is already dispersed in a sufficiently uniform condition by the stirring within the dispersion material-controlling tank 3, the medium-dispersing machine 5 and the ones accompanied therewith such as a discharge port for discharging the washing liquid 19, a valve 1 and a pump 2 may be omitted), and then a desired amount thereof is charged into the supercritical vessel 6 under the increased pressure by the pump 3.

Then, the valves V1 and V2 are closed, and the valve V4 is opened (under the condition that the valves V3, V5 and V6 are closed), and the supercritical vessel 6 is filled with the supercritical solvent. To obtain the desired temperature (a temperature which does not impair the properties of the dispersoid and is not less than the critical temperature) and the desired pressure (at a level of about two times the critical pressure), the temperature is raised by the jacket 7 and the pressure is increased by the pump P5 to bring about the supercritical state. As the above operations, an optimum operation for the dispersoid to be treated is carried out as explained with respect to the above-mentioned Figs.4 to 5.

Further, the valve V4 is closed and the valve V3 is opened. At this time, the valves V1, V2, V5 and V6 are under the closed condition, and therefore the supercritical vessel 6 is under such condition that it is shut to the external side. Then, the dispersion material compressed by the pump P4 is jetted from the nozzle 8 and the contents within the supercritical vessel 6 are stirred by a jet flow to accelerate the dispersion.

Then, the valve V3 is closed and the valve V6 is opened (the valves V1, V2, V4 and V5 are under the closed condition), to jet the dispersion into the explosion-crashing tank 10 through the jetting port 12 such as an explosion-crashing nozzle or an explosion-crashing window. The dispersion operation is further progressed by the explosion-crashing effect of the expansion of the supercritical solvent or by the collision against the collision plate equipped with a fence 13 (a countercurrent collision may be used). Since the above effect of progressing the dispersion deteriorates with reduction of the pressure in the supercritical vessel 6, the jetting of the dispersion is carried out until the pressure in the vessel reaches a level of the supercritical state while monitoring the pressure in the vessel 6.

In the explosion-crashing tank 10, the supercritical solvent is vaporized from the dispersion for separation. The supercritical solvent splashed at the section of the screen boards 11, is collected at the lower portion of the explosion-crashing tank 10, and compressed with a compressor pump P6 through a filter F2, and recovered and stored in a liquid state within the buffer tank 14, and then recycled as mentioned below.

The above dispersion is sent to a storage tank 15 by a pump P7. In the storage tank 15, heating is carried out by a jacket 16 to evaporate the unrecovered supercritical solvent for separation, followed by concentration of the dispersoid to the desired level.

The valve V3 and V6 are closed and the valves V1 and V2 are opened to fill the vessel 6 with the dispersion such as a slurry or an emulsion for the next cycle. In this case, when the filling of the supercritical solvent is conducted, the valve V5 is opened while keeping the valves V1, V2, V3, V4 and V6 in a closed condition, and firstly the supercritical solvent in the buffer tank 14 is used, and then the valve V5 is closed and the valve V4 is opened to feed the supercritical solvent for supplement of shortage.

EXAMPLES

Using carbon dioxide as a supercritical solvent, experiments for dispersing carbon black (carbon ECP manufactured by Ketchen Black International K.K.) into pure water were carried out to obtain the following Samples A to D.

Sample A...2 wt% of the above carbon black was charged into pure water, and subjected to the following operations which correspond to the operation step 3 in Figs.4(A) to (C), followed by explosion-crashing.

(20oC, 1 atm) - (5 min.) -> (20oC, 20 atm) - (5 min.) -> (50oC, 50 atm) - (5 min.) -> (60oC, 100 atm, 5 min.)-> (explosion-crashing) -> (20oC, 1 atm) (The above explanation is a brief expression of the operation steps, wherein in detail, the sample is operated by arrow direction, i.e., the sample is kept under 20°C, 1 atm for five minutes;under 20°C ,20 atm for five minutes;under 50°C, 50 atm for five minutes ; under 60°C, 100 atm for

five minutes; and then explosion-crashing operation is carried out over the sample; thus the sample is finally made under 20°C, 1 atm. The above explanation is to be applied to the operation steps of the Sample B and E.)

Sample B...2 wt% of the above carbon black was charged into pure water, and subjected to the following operations which correspond to the operation step 1 in Figs. 4(A) to (C), followed by explosion-crashing.

(20oC, 1 atm) - (7 min.) -> (20oC, 100 atm) - (8 min.)
-> (60oC, 100 atm, 5 min.) -> (explosion-crashing)

Sample C...2 wt% of the above carbon black and 3 wt% of a dispersant were charged into pure water, and then dispersion was carried out for 2 hours by using a stirring machine having four propeller blades.

Sample D...2 wt% of the above carbon black was charged into pure water, and then dispersion was carried out for 2 hours by using a stirring machine having four propeller blades.

RESULTS

The above Samples A to D were left to stand still in test tubes for 100 hours, and compared to find the differences as indicated in the explanatory drawing of Figs. 8(A) to (D).

Sample A was uniformly dispersed even after 100 hours and maintained a dispersed condition without re-agglomeration.

Sample B underwent a slight re-aggllomeration (X) or precipitation (Y), and a partial separation of water (Z), to show poor dispersed condition as compared with Sample A.

Sample C and Sample D started separation into water and carbon black from 1 hour later to show extremely poor dispersed condition.

Further, the roughness of the sample was measured by using a grindometer (JIS-K5400) (JIS=Japanese Industrial Standard) of from 0 μm to 50 μm, to find no particles having a diameter of not more than 5 μm with respect to Sample A and Sample B, whereas the presence of particles having a diameter of 33 μm was observed with respect to Sample C, and the presence of particles having a diameter of 40 μm was observed with respect to Sample D.

As is apparent from the above results, the excellent dispersed condition can be obtained by the dispersion method employing the supercritical state of the present invention and the apparatus thereof.

Further, Sample E as indicated below was prepared for the confirmation of the explosion-crashing effect according to the present invention.

Sample E...2 wt% of the above carbon black was charged into pure water, and subjected to the following operations which correspond to the operation step 3 in Figs.4(A) to (C), followed by mild reduction of pressure (namely, no explosion-crashing was carried out).

(20oC, 1 atm) - (5 min.) -> (20oC, 20 atm) - (5min.) -> (50oC, 50 atm) - (5 min.) -> (60oC, 100 atm, 5 min.) - (60 min.) -> (20oC, 1 atm)

RESULTS

Using a particle size distribution-measuring machine using a light scattering method (Laser Micronsyzer, Model PRO-7000S, manufactured by Kabushiki Kaisha Seishin Kigyo), the particle size distribution of the carbon black in each of the above-mentioned Samples A to D and in the dispersion of Sample E was measured, and the results as indicated in Fig.9 were obtained. As is apparent from the results of measurement, Samples A and B obtained by the explosion-crashing shows highly uniform particle size distribution as compared with Sample E, whereby the effects of the explosion-crashing were confirmed.

According to the present invention as constituted above, the dispersoid and solvent are mixed, and this mixture is mixed with a supercritical fluid in the supercritical vessel,and then the supercritical mixture is jetted in the explosion-crashing tank for explosion-crashing. By such a method, in a solid (fine particles)-liquid system dispersion, the supercritical fluid in a low density condition (diffusion coefficient is large and viscosity is small) penetrates into spaces of aggregate of the fine particles or pores of the fine particles, and then the pressure is increased to make the density of the fluid high (intermolecular action is large and wettability to the fine particles is high) to accelerate the formation of primary particles of fine particles, and further rapid reduction of pressure (release to atmospheric pressure) is carried out to make the density of the fluid small (the volume is made large), whereby effective dispersion can be carried out and reagglomeration after the dispersion is unlikely to take place. Further, in a liquid (dispersoid)-liquid (water) system dispersion, by using a high solubility under a high density condition, the supercritical fluid is dissolved into the droplets of dispersoid present in the liquid (water) (in some case, a homogeneous condition of water-dispersoid-supercritical fluid),and then rapid reduction of pressure is carried out (release to atmospheric pressure) to rapidly reduce the density (the volume is made large), whereby the dispersion is accelerated and re-agglomeration is unlikely to take place. In the case of a slurry having a high viscosity, the introduction of above supercritical fluid can remarkably reduce the viscosity, by which the jetting from the nozzle or the like is made for easy crashing and dispersion.

Further, the operation for accelerating the wetting of the surface of the solid particles or the inside of pores with the supercritical solvent and for the formation of dispersed condition of primary particles, can properly be made by a computer control by selecting the optimum operation route of the temperature and pressure. By such effects, further improved dispersion can be provided by the collision portion of the explosion-crashing

tank at the time of releasing to the atmospheric pressure, and further the supercritical solvent can be recovered for recycling, whereby resources-saving type dispersion system can be obtained.

Claims

1. A dispersion method using a supercritical state, which comprises feeding a mixture of a dispersoid and a solvent into a supercritical vessel, feeding a supercritical solvent into the supercritical vessel, heating and compressing the supercritical solvent to convert it from a gaseous phase state to a supercritical fluid, mixing the mixture and the supercritical fluid in the supercritical vessel, then introducing the supercritical mixture of the mixture and the supercritical fluid to an explosion-crashing tank, to release the supercritical mixture to atmospheric pressure and collide the supercritical mixture to a collision portion, thereby dispersing the dispersoid.

2. The dispersion method according to Claim 1, wherein the supercritical solvent is separated from the supercritical mixture in the explosion-crashing tank, and the separated supercritical solvent is recovered and fed to the supercritical vessel.

3. The dispersion method according to Claim 1, wherein the mixture of the dispersoid and solvent is a slurry having a solid dispersoid suspended in a solvent such as an organic solvent or water.

4. The dispersion method according to Claim 1, wherein the mixture of the dispersoid and solvent is an emulsion having a liquid type solute suspended in a solvent such as an organic solvent or water.

5. The dispersion method according to Claim 1, wherein the mixture of the dispersoid and solvent is a slurry having solid and liquid dispersoids suspended in a liquid solvent.

6. A dispersion method using a supercritical state, which comprises introducing a supercritical fluid into a mixture of a dispersoid and a solvent to reduce the viscosity, jetting the reduced viscosity mixture from a pore under reduced pressure, imparting the dispersoid a volume-expansion action, a high shearing action and an impact action to crash and disperse the dispersoid.

7. A dispersing apparatus, which comprises a supercritical vessel having a feeding portion for charging a mixture of a dispersoid and a solvent, a feeding portion for charging a supercritical solvent and a flow-out port; a heating and compressing means for converting the supercritical solvent within the supercritical vessel to a supercritical fluid; a stirring means for stirring the supercritical mixture of the mixture and the supercritical fluid in the supercritical vessel; an explosion-crashing tank which is connected to the flow-out port of the supercritical vessel and has a jetting port for releasing the supercritical mixture to atmospheric pressure; and a storage tank for storing a dispersion obtained in the explosion-crashing tank.

8. The dispersing apparatus according to Claim 7, wherein a buffer tank for recovering the supercritical solvent separated in the explosion-crashing tank is connected to the explosion-crashing tank and the buffer tank is connected to the feeding portion for feeding the supercritical solvent of the supercritical vessel.

9. The dispersing apparatus according to Claim 7, wherein a preliminary mixing apparatus for preliminarily mixing the dispersoid and the solvent, is connected to the feeding portion for feeding the mixture of a dispersoid and a solvent of the supercritical vessel.

10. The dispersing apparatus according to Claim 7, wherein the heating and compressing means is operated so that the supercritical solvent is converted from a gaseous phase state to a supercritical fluid.

11. The dispersing apparatus according to Claim 7, wherein the stirring means comprises a nozzle disposed toward the inside of the supercritical vessel and a circulating pump for circulating the supercritical mixture flown out of the supercritical vessel to the nozzle.

12. The dispersing apparatus according to Claim 7, wherein the stirring means has an ultrasonic-generating means disposed at the supercritical vessel to apply ultrasonic wave in the supercritical vessel.

13. The dispersing apparatus according to Claim 7, wherein the stirring means is a vibration plate or rotation blades disposed at the supercritical vessel which is actuated by an electromagnetic coil provided at the external portion of the supercritical vessel and a shifting magnetic field generated by the electromagnetic coil.

14. The dispersing apparatus according to Claim 7, wherein the explosion-crashing tank comprises a collision portion to which the supercritical mixture is collided.

15. The dispersing apparatus according to Claim 14, wherein the jetting port for jetting the supercritical mixture disposed at the explosion-crashing tank is

an explosion-crashing nozzle, and the collision portion is arranged vertically to the nozzle.

16. The dispersing apparatus according to Claim 14, wherein the jetting port for jetting the supercritical mixture disposed at the explosion-crashing tank is an explosion-crashing window, and the collision portion is arranged into a semi-spherical form to the window.

17. The dispersing apparatus according to Claim 7, wherein the jetting port for jetting the supercritical mixture disposed at the explosion-crashing tank is a pair of nozzles oppositely disposed to collide the supercritical mixture each other, the nozzles constituting the collision portion.

18. A dispersing apparatus which comprises a jetting port having a pore from which a mixture of a dispersoid and a solvent, having a supercritical fluid introduced there-into for reduction of a viscosity, is jetted under a reduced pressure, and a collision portion for imparting an impact to the dispersoid jetted from the jetting port.

19. The dispersing apparatus according to Claim 18, wherein the collision portion is a collision plate arranged oppositely to the jetting port.

20. The dispersing apparatus according to Claim 18, wherein the collision portion is a countercurrent collision portion at which a pair of dispersoids are jetted oppositely and collided each other.

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20

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40

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50

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FIG. 1

FIG. 1

(C)

(D)

• supercritical solvent

FIG. 2

(A)

(B)

(C)

(D)

FIG. 3

(A)

(B)

(C)

F I G. 4

FIG. 5

F I G. 6

(A)

water,org.
solvent

solute

d

d

30

6

P4

P5

10

(B)

supercritical
fluid + solute

water,org.
solvent

6

(B-1)

8
9

P4

P5

10

supercritical
solvent

(B-2)

6

water,org.
solvent +
solute +
supercritical
solvent

b

b

d

b

d

b

• supercritical solvent

FIG. 6

(C)

supercritical solvent

(D)

F I G. 7

FIG. 8

(A)

(B)

(C)

(D)
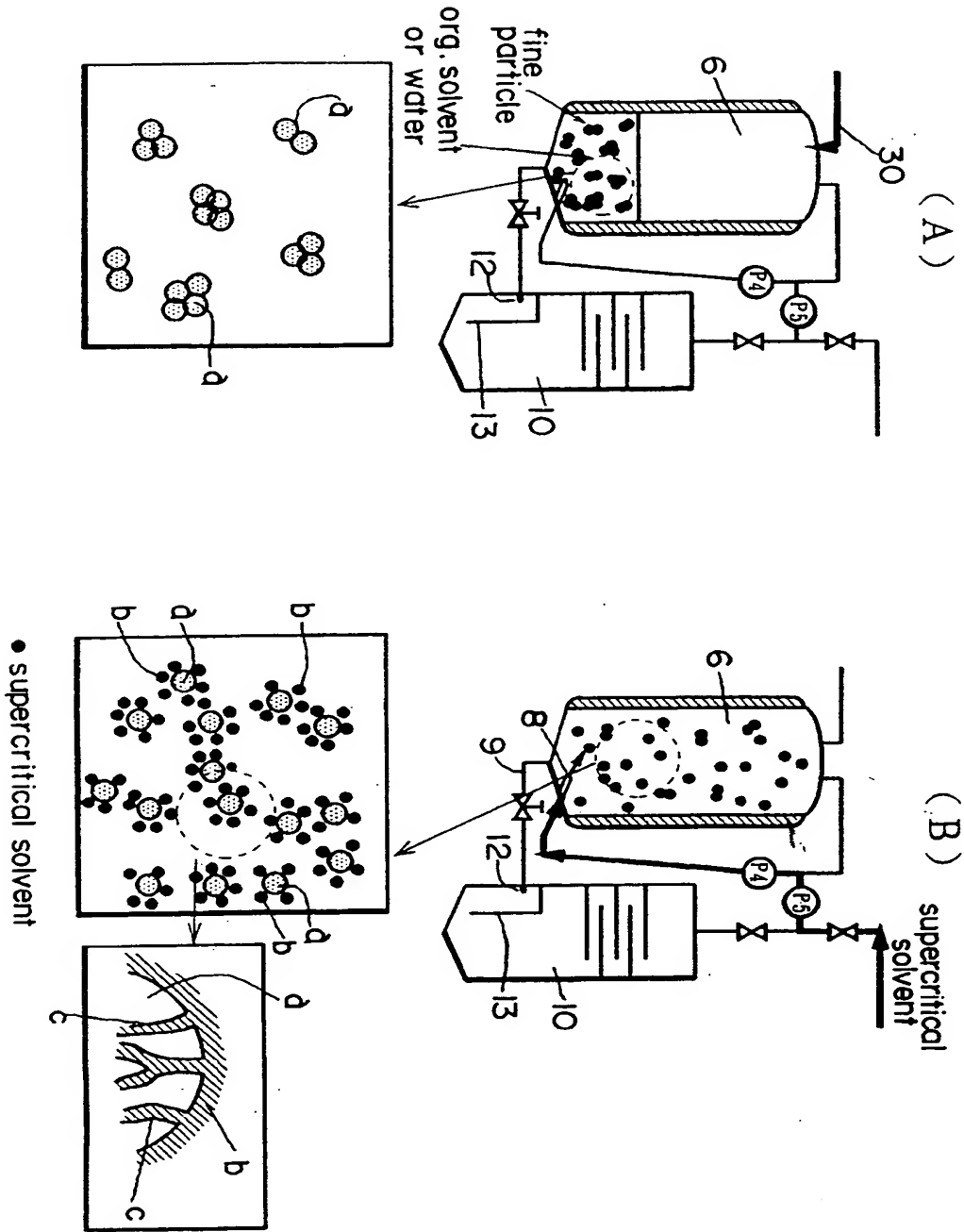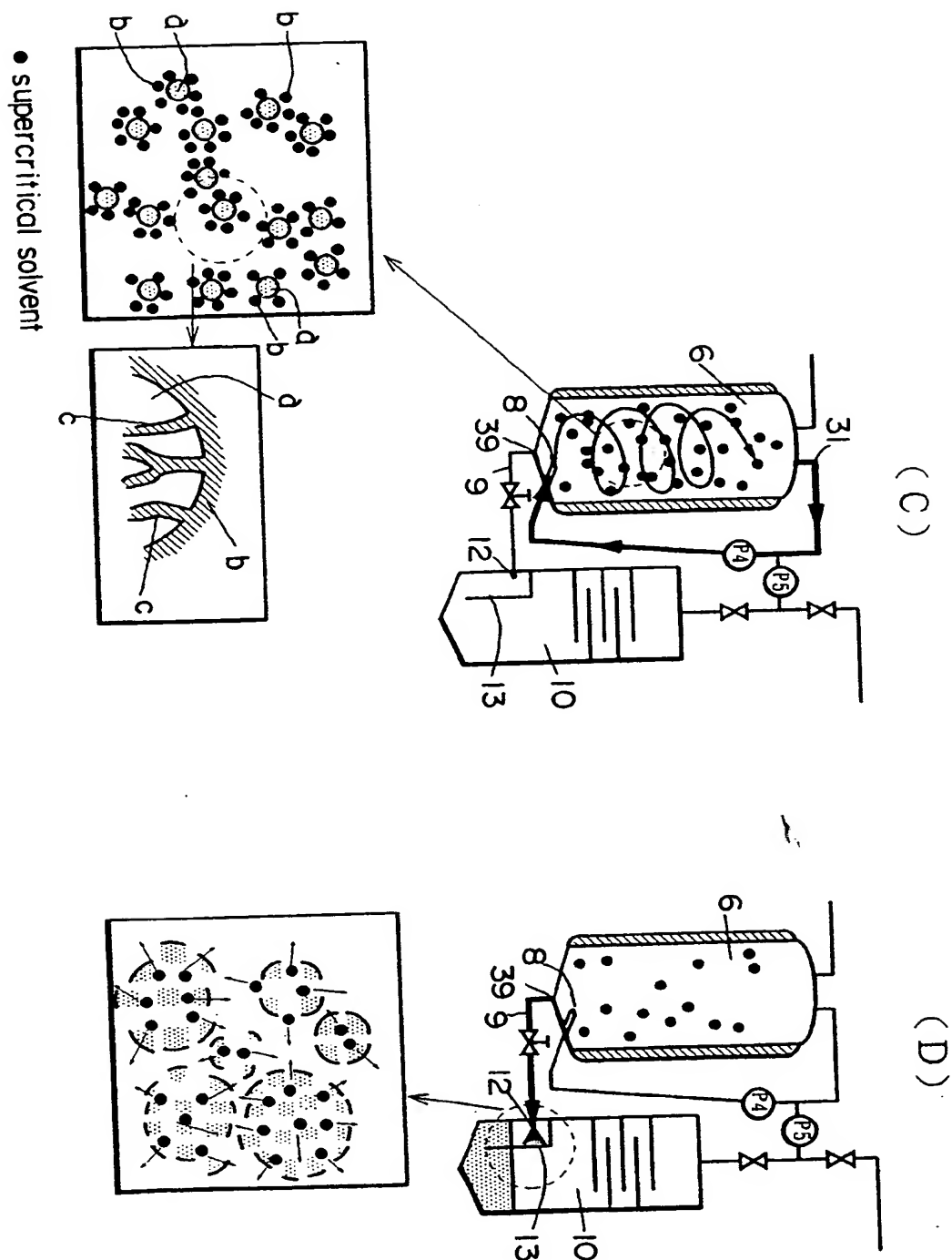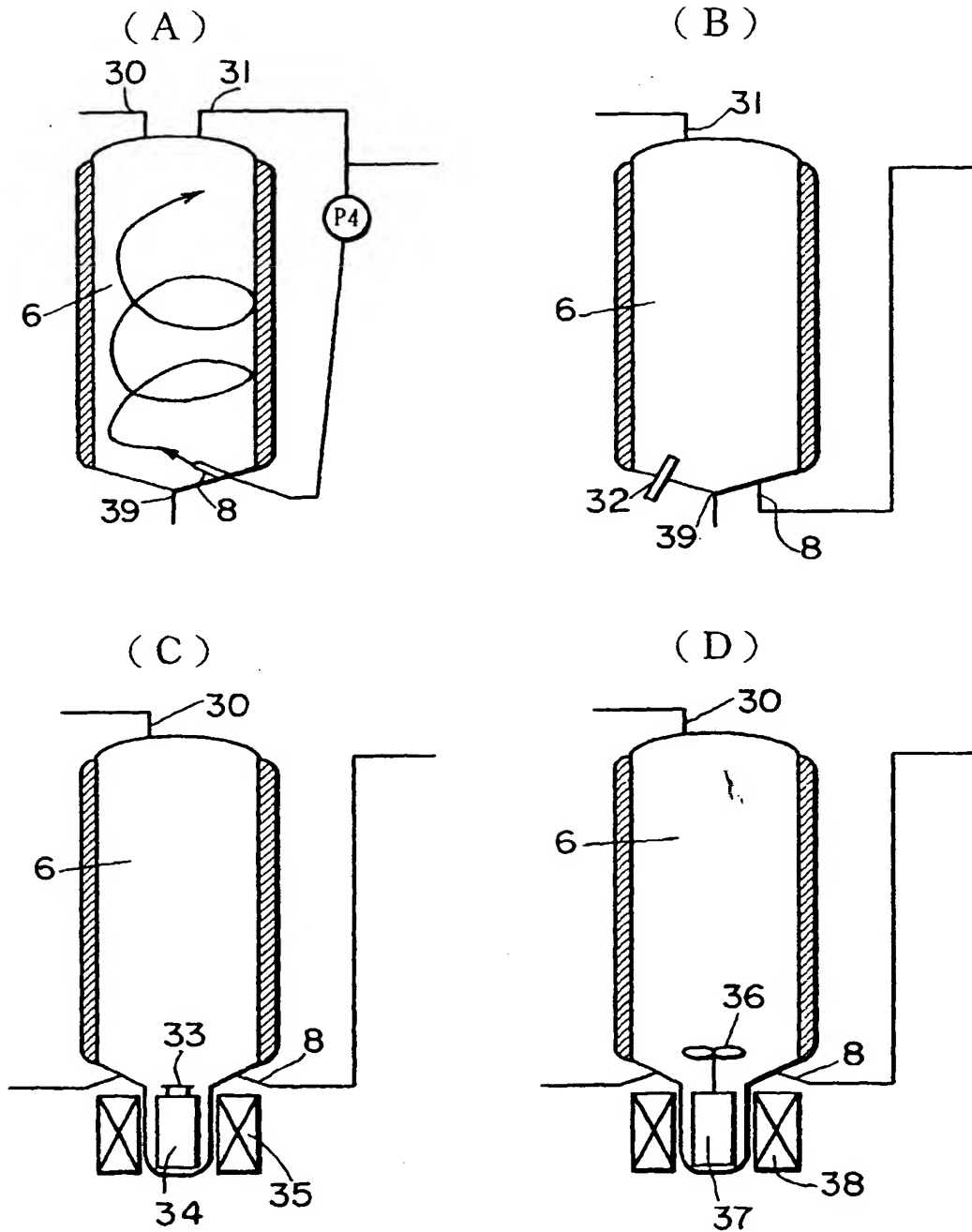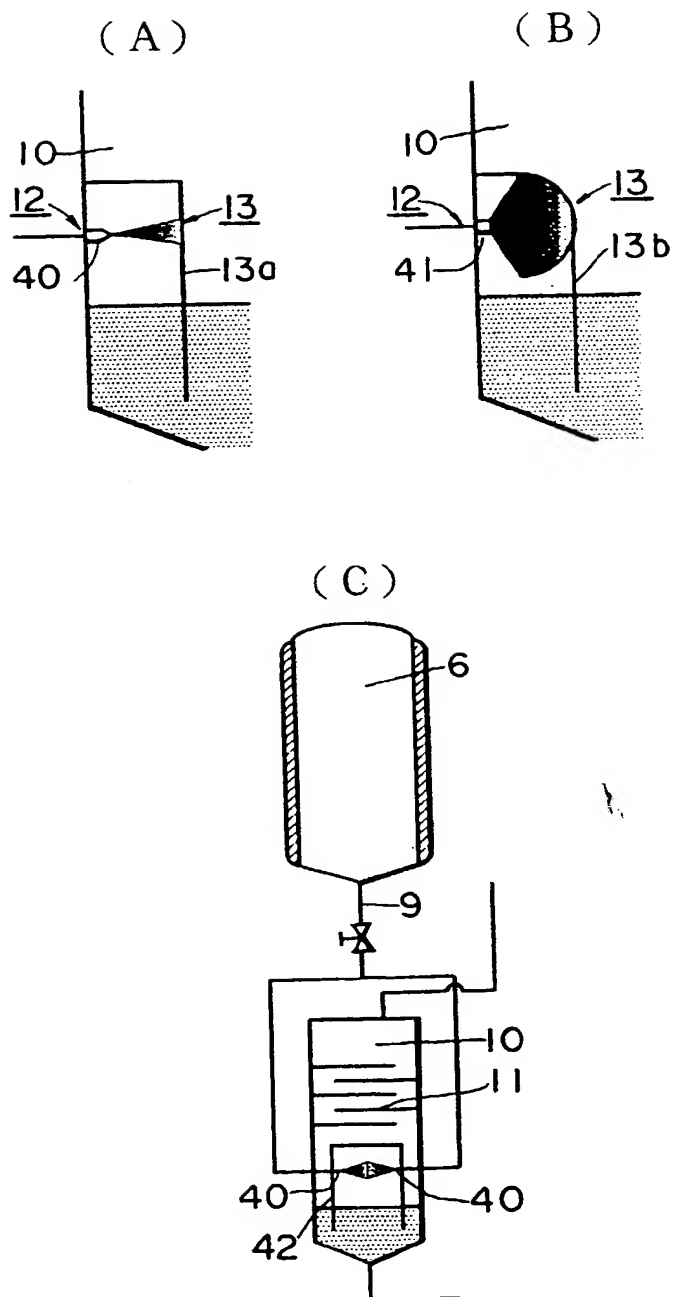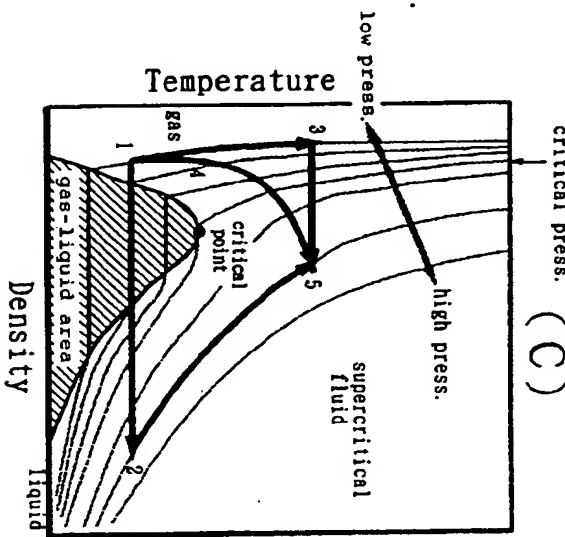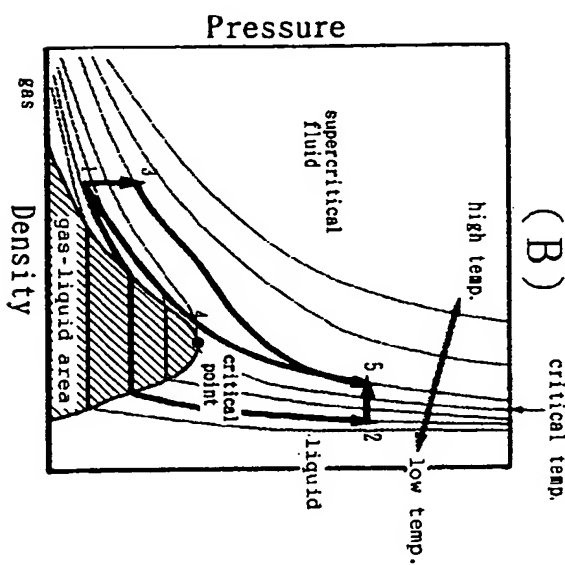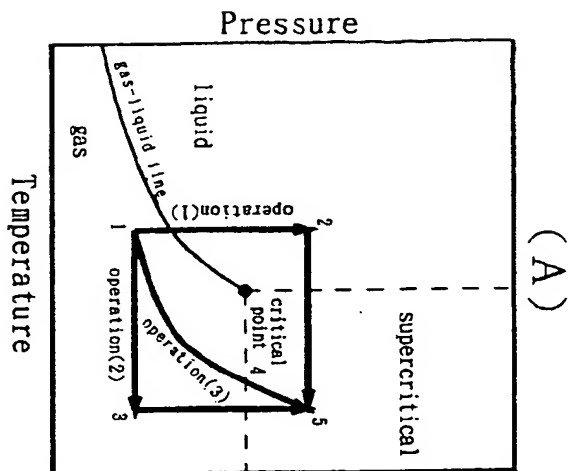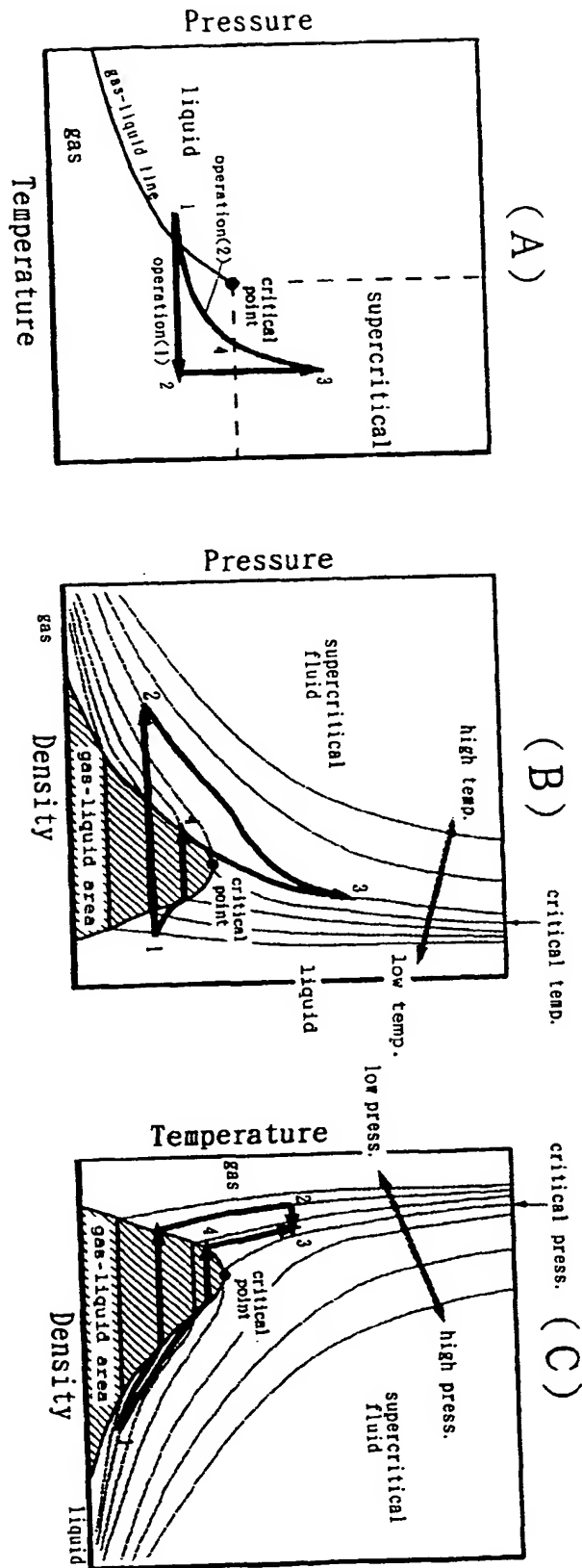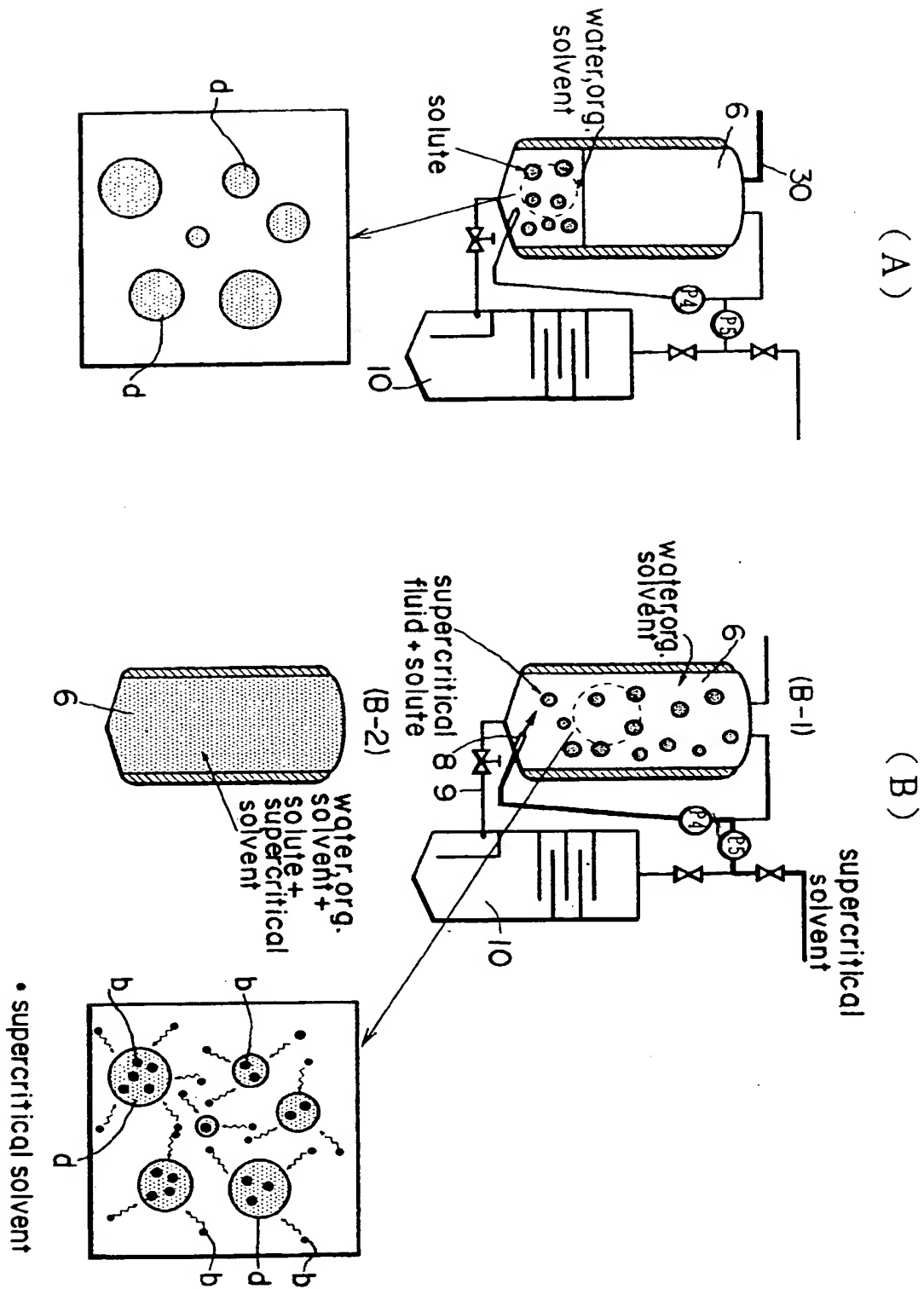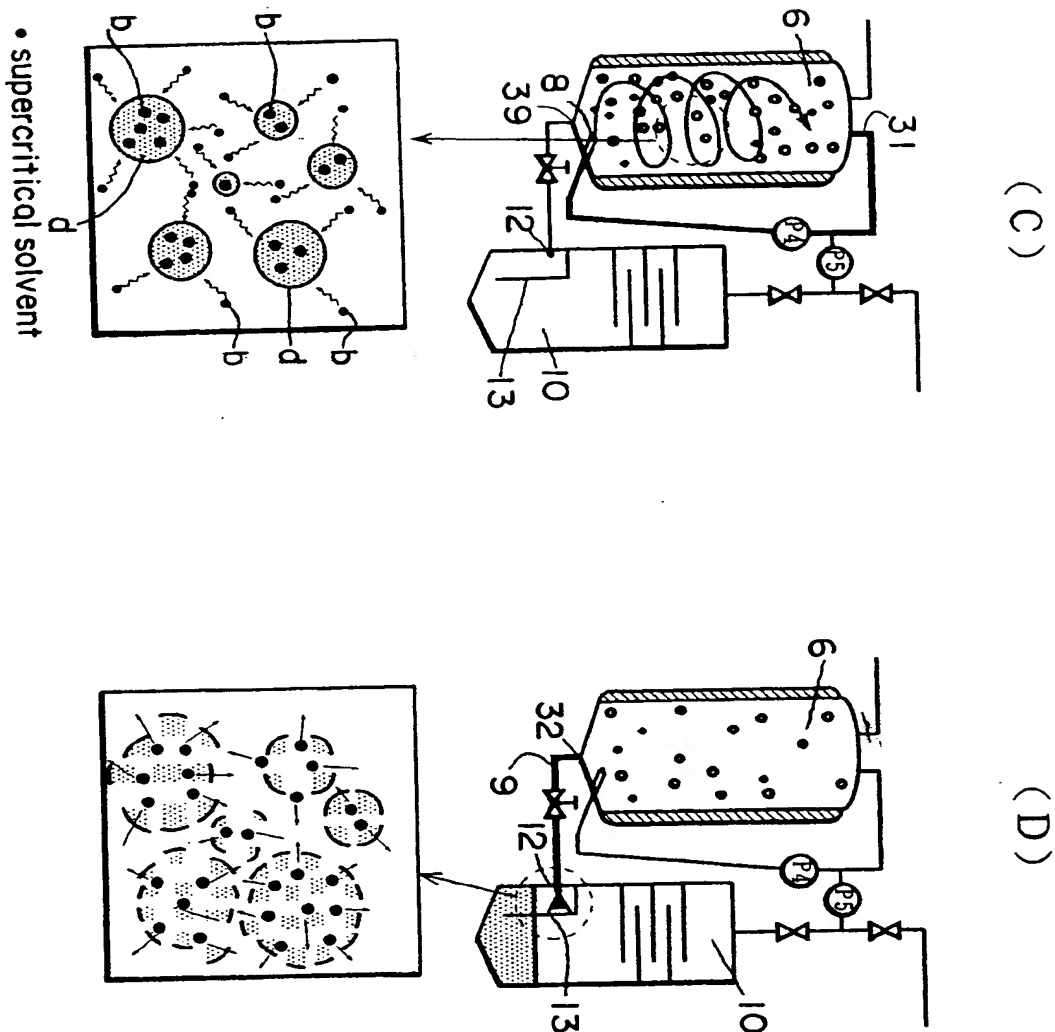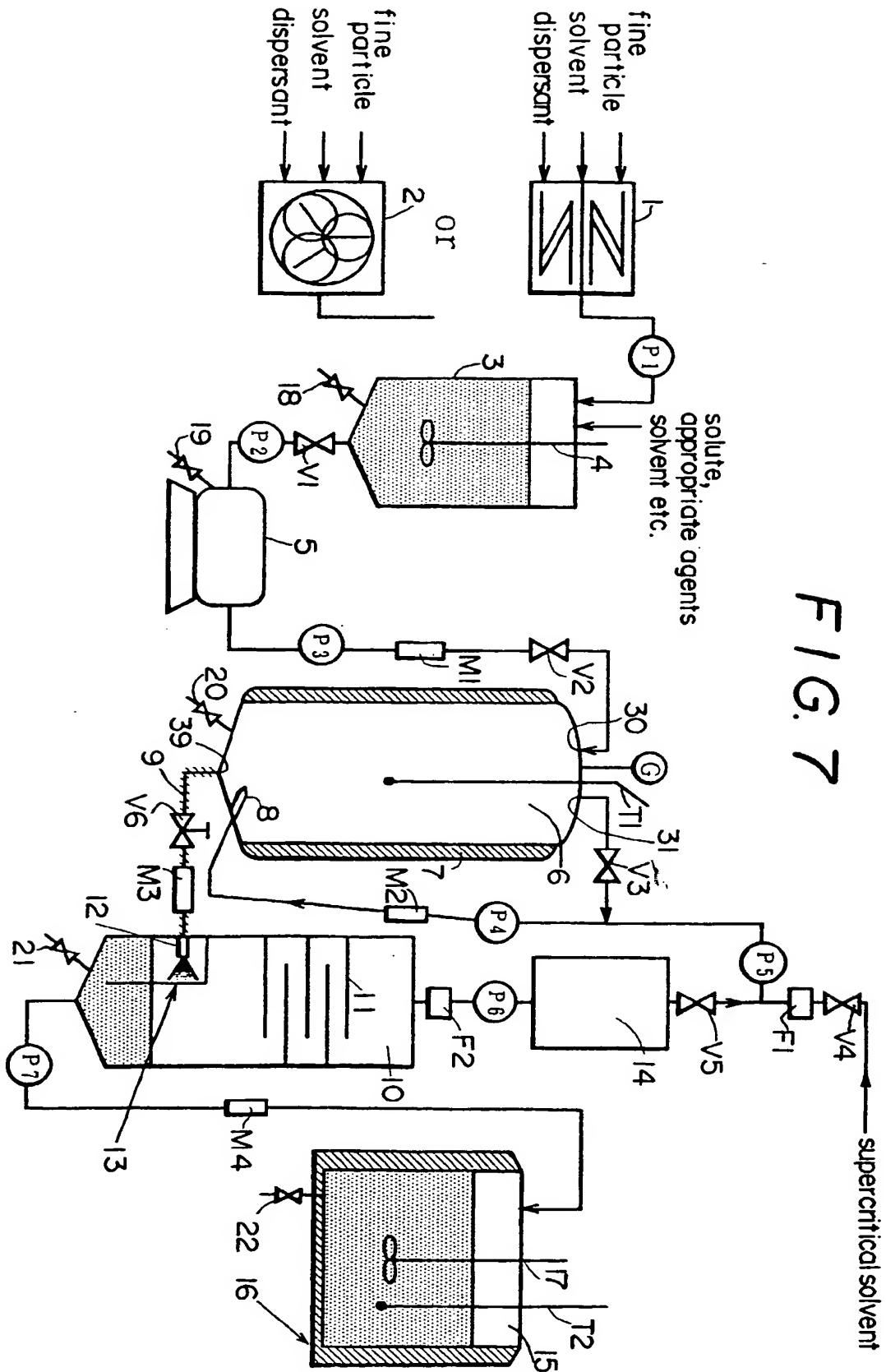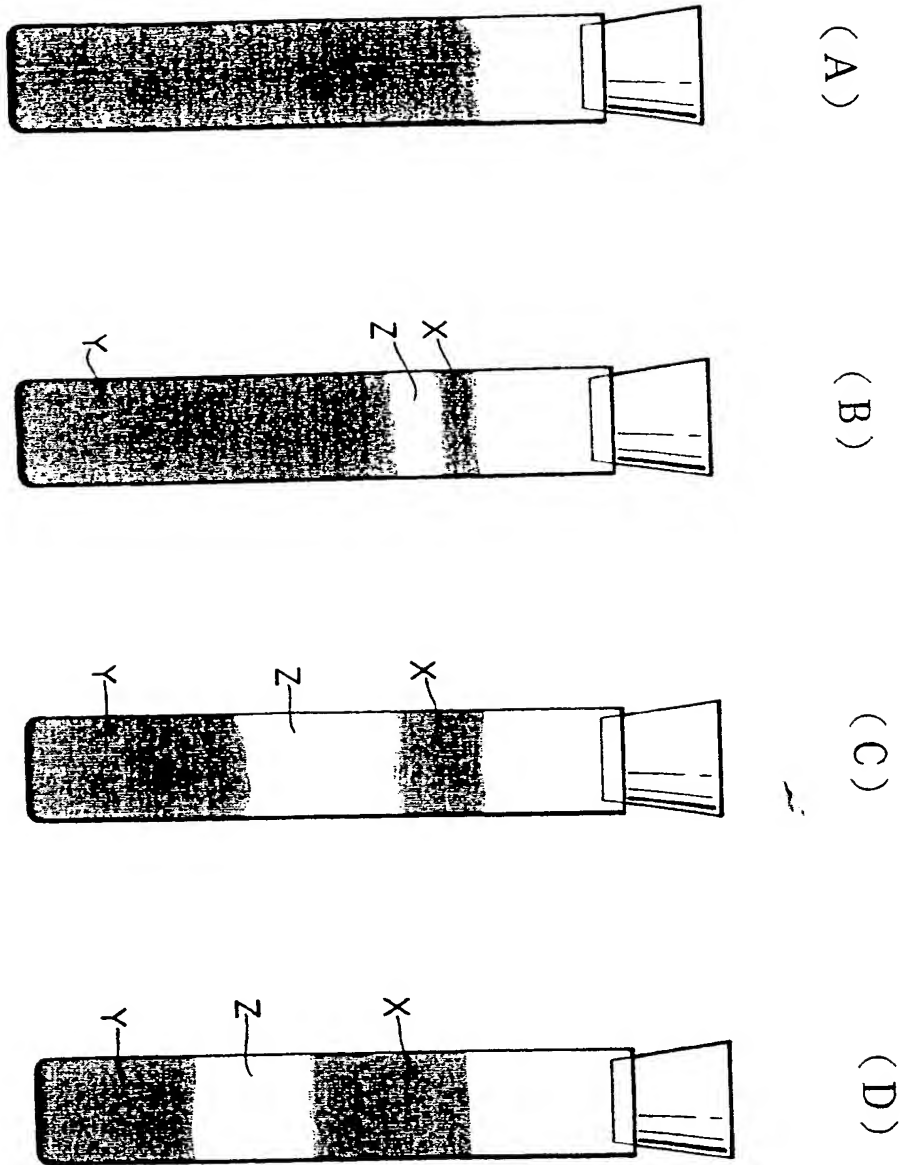
FIG. 9
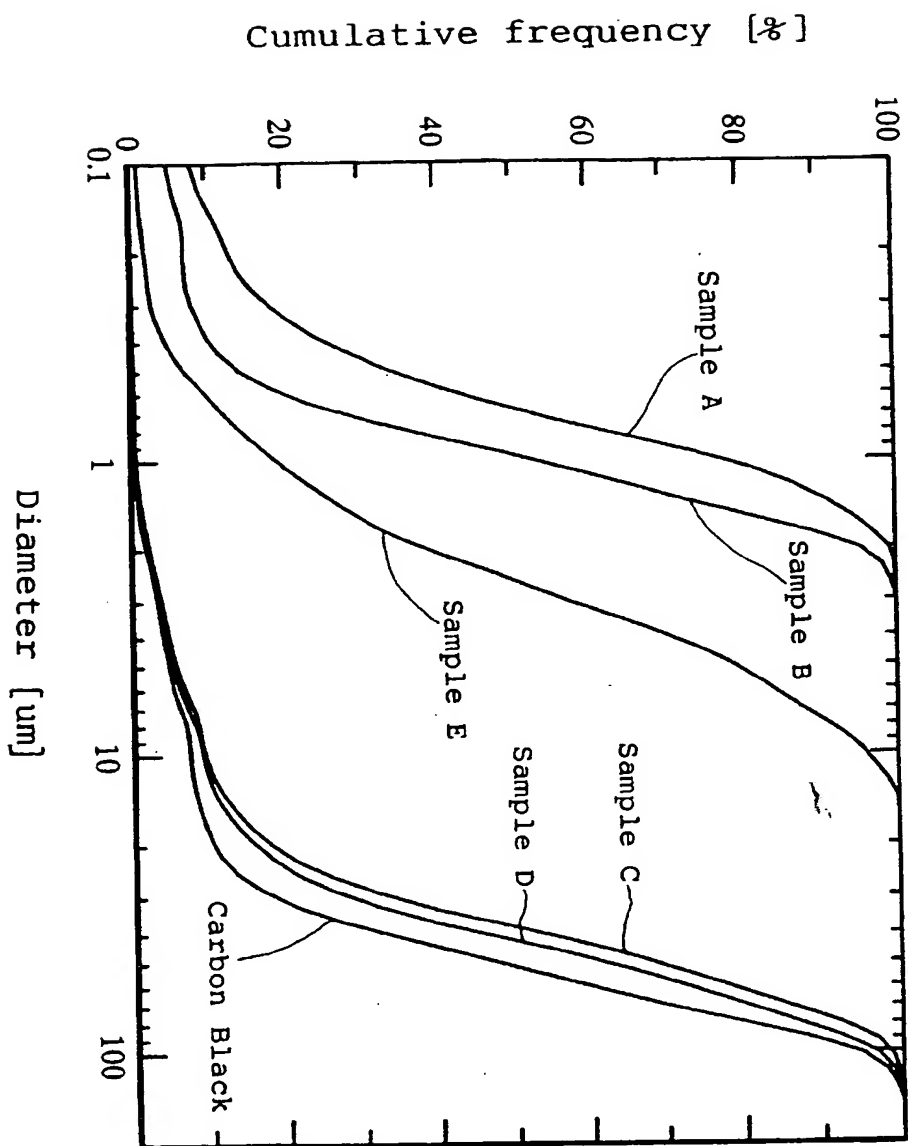
European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 97 11 4702

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 5 487 965 A (ODELL PETER G) 30 January 1996 * abstract * * column 10, line 5-45 * * column 10, line 66 - column 11, line 8 * ---	1,6,18	B01F3/12
A	US 4 734 451 A (SMITH RICHARD D) 29 March 1988 * the whole document * -----		

TECHNICAL FIELDS
SEARCHED (Int.Cl.6)

B01F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	22 April 1998	Hoffmann, A

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